

Non-local kinetic theory of inhomogeneous liquid mixtures

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In this work we investigate the dynamical properties of a mixture of mutually interacting spherical molecules of different masses and sizes. From an analysis of the microscopic laws governing the motion of the molecules we derive a set of non-local self-consistent equations for the singlet phase-space distribution functions. The theory is shown to reproduce the hydrodynamic equations for the densities of each species, the total momentum and the local temperature. The non ideal gas interaction term is separated into a contribution due to the repulsive part, which is treated by means of the revised Enskog theory for hard spheres, and an attractive contribution treated within the random phase approximation. The present formulation accounts for the effects of the density and velocity inhomogeneities both on the thermodynamic and transport properties of the fluid.

In a special limit, where one species is massive and diluted, the theory leads to a description which is formally identical to the dynamic density functional equation governing the time evolution of a colloidal system. The derivation also determines the dependence of the friction coefficient, appearing in the dynamic density functional theory, on the microscopic parameters of the solvent. However, the predicted value takes into account only the collisional contributions to the friction and not the Stokes friction of hydrodynamic origin, suggesting that velocity correlations should be incorporated in a more complete treatment.

I. INTRODUCTION

Spatially inhomogeneous systems on mesoscopic length scales can generate properties which do not appear in bulk materials, offering new perspectives for future applications. A variety of tools have been utilized to study the properties of fluids near substrates and liquid interfaces in terms of molecular forces, ranging from new experimental techniques to numerical algorithms and theoretical approaches [1–4, 6, 13].

It is an understatement to say that, since its appearance in 1979, the *Manifesto* [7] of density functional theory (DFT) has strongly influenced the studies in the field of classical inhomogeneous fluids. In this approach the equilibrium density profile is determined by a functional derivative of a non-local Helmholtz free energy functional. An exact theorem states that such an equilibrium profile minimizes the grand potential of the system and is unique. This fact renders the method extremely appealing and provides a great help in finding good approximate Helmholtz functionals in a variety of cases.

Regarding out of equilibrium systems, we do not have such useful theorems [8] and a time dependent extension of these methods, the dynamical density functional theory (DDFT), has been applied on phenomenological grounds [9, 10]. As shown by means of comparisons with numerical simulations, DDFT is able to capture the over-damped dynamics of suspensions, but does not account for the richer dynamics of molecular fluids [11–13]. Although some hydrodynamic aspects, such as the presence of a drift in the solvent or inertial corrections [14–16], can be included in the DDFT, a full treatment of these effects requires a different approach. In order to capture the isothermal hydrodynamic behavior, describing the long length and long time scale behavior of fluids, one must consider the momentum density in addition to the mass density. Hydrodynamics, developed much earlier than Kinetic theory and without any knowledge of the underlying microscopic structure of liquids, but using only phenomenological arguments and conservation laws [17], represents a universal theory of fluid behavior. With this remark we want to stress the fact that, in constructing a dynamical description of a fluid valid both at molecular and macroscopic scales, we must be consistent with the assumptions which rendered classical hydrodynamics such a successful theory of liquids. In other words, symmetries and mass and momentum conservation laws must be exactly preserved even when necessary and unavoidable approximations are introduced.

When a liquid is treated as a mechanical continuum, it is relatively simple to find a closed set of governing hydrodynamic equations for the relevant fields with the help of the so-called phenomenological constitutive relations. However, when the physical inhomogeneities become of the same order of magnitude as the molecular scales, one is forced to adopt a microscopic description [18]. The challenge is to extend macroscopic concepts such as pressure, viscosity, diffusivity and thermal conductivity to situations, where matter is confined to narrow spaces or is heterogeneous. All these properties assume a non-local dependence on the controlling fields and this fact renders the theory particularly challenging.

The present paper is organized as follows: in Sec. II we introduce the model and the evolution equations for the distribution functions of the multi-component system. Numerical solutions of the transport equations are possible by means of the Lattice Boltzmann technique [19] as discussed elsewhere [20–23]. In Sec. III we analyze the predictions of the theory concerning the equilibrium and non equilibrium behavior of the model and give the relevant formulae to compute the pressure and the transport coefficients. In Sec. IV we mimic a colloidal suspension by specializing the discussion to a hard-sphere binary mixture, composed of a low-concentration heavy species and a high concentration light species. From this non primitive model we obtain an equation for the evolution of the heavy species alone very similar to the DDFT equation. This heuristic derivation also shows the limits of approaches based on the neglect of velocity correlations. Finally in Sec. V we present some conclusions and perspectives.

II. THEORY

We consider an M -component fluid, whose species, denoted by the label $\alpha = 1, M$, have masses m_α and interact with pair additive, centrally symmetric potentials $U^{\alpha\beta}(r)$ and external forces \mathbf{F}_α . We describe the statistical evolution of the system by means of the so-called BBGKY hierarchy of equations [24], whose first M equations involve the singlet phase space distribution functions, $f^\alpha(\mathbf{r}, \mathbf{v}, t)$ and the two particle distribution functions, $f_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}', \mathbf{v}, \mathbf{v}', t)$:

$$\partial_t f^\alpha(\mathbf{r}, \mathbf{v}, t) + \mathbf{v} \cdot \nabla f^\alpha(\mathbf{r}, \mathbf{v}, t) + \frac{\mathbf{F}^\alpha(\mathbf{r})}{m^\alpha} \cdot \frac{\partial}{\partial \mathbf{v}} f^\alpha(\mathbf{r}, \mathbf{v}, t) = \sum_\beta \Omega^{\alpha\beta}(\mathbf{r}, \mathbf{v}, t) \quad (1)$$

where the interaction term $\Omega^{\alpha\beta}$ is given by:

$$\Omega^{\alpha\beta}(\mathbf{r}, \mathbf{v}, t) = \frac{1}{m^\alpha} \nabla_v \cdot \int d\mathbf{v}' \int d\mathbf{r}' \nabla_r U^{\alpha\beta}(\mathbf{r} - \mathbf{r}') f_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}', \mathbf{v}, \mathbf{v}', t). \quad (2)$$

The evolution equations for the singlet distributions involve the two particle distributions and these in turn involve the three-particle distributions. In order to make some progress one needs to approximate these higher order distributions, using some physically motivated prescription. A popular closure ansatz allowing to reduce the BBGKY equations [24] to a closed set of equations for the singlet distributions is the following:

$$f_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}', \mathbf{v}, \mathbf{v}', t) \simeq g_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t) f^\alpha(\mathbf{r}, \mathbf{v}, t) f^\beta(\mathbf{r}', \mathbf{v}', t), \quad (3)$$

where $g_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t)$ is the local equilibrium pair distribution function. The approximation (3) incorporates static correlations correctly, but neglects velocity correlations, through the lack of velocity dependence in $g_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t)$. We shall comment later on the consequences of such an ansatz. We assume that the interaction potential between two particles can be separated into a short-range strongly repulsive and a longer range attractive contribution, so that the interaction process results in a combination of almost instantaneous, hard core collisions and small velocity changes induced by the weak attractive field:

$$\Omega^{\alpha\beta}(\mathbf{r}, \mathbf{v}, t) = \Omega_{rep}^{\alpha\beta}(\mathbf{r}, \mathbf{v}, t) + \Omega_{att}^{\alpha\beta}(\mathbf{r}, \mathbf{v}, t). \quad (4)$$

The repulsive part of $\Omega_{rep}^{\alpha\beta}$ is treated using the Revised Enskog theory of Ernst and van Beijeren [25–29] for hard-sphere mixtures of diameters $\sigma_{\alpha\beta}$, which neglects velocity correlations for two particles about to collide, as in Boltzmann theory, but includes the configurational correlations resulting from the finite size of the particles via the pair correlation function at contact:

$$\begin{aligned} \Omega_{rep}^{\alpha\beta}(\mathbf{r}, \mathbf{v}^\alpha, \mathbf{v}^\beta, t) &= \sigma_{\alpha\beta}^2 \int d\mathbf{v}^\beta \int d\hat{\mathbf{s}} \Theta(\hat{\mathbf{s}} \cdot \mathbf{v}_{\alpha\beta}) (\hat{\mathbf{s}} \cdot \mathbf{v}_{\alpha\beta}) \times \\ &\left\{ g_{\alpha\beta}(\mathbf{r}, \mathbf{r} - \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) f^\alpha(\mathbf{r}, \bar{\mathbf{v}}^\alpha, t) f^\beta(\mathbf{r} - \sigma_{\alpha\beta} \hat{\mathbf{s}}, \bar{\mathbf{v}}^\beta, t) \right. \\ &\left. - g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) f^\alpha(\mathbf{r}, \mathbf{v}^\alpha, t) f^\beta(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, \mathbf{v}^\beta, t) \right\}, \end{aligned} \quad (5)$$

where $\Theta(x)$ is the Heaviside function, $\mathbf{v}_{\alpha\beta} = (\mathbf{v}^\alpha - \mathbf{v}^\beta)$, while $\bar{\mathbf{v}}^\alpha$ and $\bar{\mathbf{v}}^\beta$ are scattered velocities given by

$$\begin{aligned} \bar{\mathbf{v}}^\alpha &= \mathbf{v}^\alpha - \frac{2m^\beta}{m^\alpha + m^\beta} (\hat{\mathbf{s}} \cdot \mathbf{v}_{\alpha\beta}) \hat{\mathbf{s}} \\ \bar{\mathbf{v}}^\beta &= \mathbf{v}^\beta + \frac{2m^\alpha}{m^\alpha + m^\beta} (\hat{\mathbf{s}} \cdot \mathbf{v}_{\alpha\beta}) \hat{\mathbf{s}} \end{aligned} \quad (6)$$

and $\hat{\mathbf{s}}$ is the unit vector directed from particle α to particle β . The quantities $g_{\alpha\beta}(\mathbf{r}, \mathbf{r} \pm \sigma_{\alpha\beta}\hat{\mathbf{s}})$ are the inhomogeneous hard sphere pair correlation functions evaluated when the particles of species α and β are at contact distance $\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2$. The attractive term has the random phase approximation [24] expression:

$$\Omega_{attr}^{\alpha\beta}(\mathbf{r}, \mathbf{v}, t) = -\frac{\mathbf{G}^{\alpha\beta}(\mathbf{r}, t)}{m^\alpha} \cdot \nabla_{\mathbf{v}} f^\alpha(\mathbf{r}, \mathbf{v}, t) \quad (7)$$

where $\mathbf{G}^{\alpha\beta}$ are the molecular fields

$$\mathbf{G}^{\alpha\beta}(\mathbf{r}, t) = -\int d\mathbf{r}' n^\beta(\mathbf{r}', t) g_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t) \nabla_{\mathbf{r}} U_{attr}^{\alpha\beta}(\mathbf{r} - \mathbf{r}') \quad (8)$$

and n^β the number density of species β . Even with approximations (5) and (7) the full solution of eq. (1) is exceedingly difficult and can be found only in some special cases of limited interest. In order to encompass this problem many authors adopted simpler forms of the interaction term. Among these forms, a very popular recipe is represented by the BGK model [30] consisting in replacing $\Omega^{\alpha\beta}$ by a relaxation term. For collisions between particles belonging to the same species one chooses:

$$\Omega_{BGK}^{\alpha\alpha} = -\omega_{\alpha\alpha}(f^\alpha(\mathbf{r}, \mathbf{v}, t) - \psi^\alpha(\mathbf{r}, \mathbf{v}, t)) \quad (9)$$

and for collisions between unlike particles:

$$\Omega_{BGK}^{\alpha\bar{\alpha}} = -\omega_{\alpha\bar{\alpha}}(f^\alpha(\mathbf{r}, \mathbf{v}, t) - \bar{\psi}^\alpha(\mathbf{r}, \mathbf{v}, t)) \quad (10)$$

where ψ^α is the local equilibrium distribution for species α :

$$\psi^\alpha(\mathbf{r}, \mathbf{v}, t) = n^\alpha(\mathbf{r}, t) \left[\frac{m^\alpha}{2\pi k_B T} \right]^{3/2} \exp\left(-\frac{m^\alpha(\mathbf{v} - \mathbf{u}(\mathbf{r}, t))^2}{2k_B T} \right). \quad (11)$$

and the functions $\bar{\psi}^\alpha$ and the frequencies $\omega_{\alpha\bar{\alpha}}$ have to be modeled to account for collisions between particles of different species [31].

The BGK approximation is based on the idea that the system after few molecular collisions reaches a state of local thermodynamic equilibrium, where the distributions depend on space and time only through the hydrodynamic variables of the system, $\rho^\alpha(\mathbf{r}, t)$, $\mathbf{u}(\mathbf{r}, t)$, $T(\mathbf{r}, t)$, partial mass densities, average velocity and temperature, respectively. These variables are defined in terms of the distributions as:

$$\rho^\alpha(\mathbf{r}, t) = m^\alpha n^\alpha(\mathbf{r}, t) = m^\alpha \int d\mathbf{v} f^\alpha(\mathbf{r}, \mathbf{v}, t), \quad (12)$$

$$\mathbf{u}^\alpha(\mathbf{r}, t) = \frac{1}{n^\alpha(\mathbf{r}, t)} \int d\mathbf{v} \mathbf{v} f^\alpha(\mathbf{r}, \mathbf{v}, t), \quad (13)$$

and

$$T(\mathbf{r}, t) = \frac{1}{3n(\mathbf{r}, t)} \sum_{\alpha} m^\alpha \int d\mathbf{v} (\mathbf{v} - \mathbf{u})^2 f^\alpha(\mathbf{r}, \mathbf{v}, t) \quad (14)$$

with total density given by $n(\mathbf{r}, t) = \sum_{\alpha} n^\alpha(\mathbf{r}, t)$, barycentric velocity by $\mathbf{u}(\mathbf{r}, t) = \sum_{\alpha} \rho^\alpha(\mathbf{r}, t) \mathbf{u}^\alpha(\mathbf{r}, t) / \rho(\mathbf{r}, t)$ and global density $\rho(\mathbf{r}, t) = \sum_{\alpha} \rho^\alpha(\mathbf{r}, t)$. With the help of the BGK ansatz one easily derives the hydrodynamic equations for the conserved variables $\rho^\alpha(\mathbf{r}, t)$, $\rho \mathbf{u}(\mathbf{r}, t)$ and the energy and via the Chapman-Enskog analysis [32] the transport coefficients. Unfortunately, the method gives an oversimplified picture of the thermodynamic properties of the system, which turn out to be the same as those of an ideal gas, since $\Omega_{BGK}^{\alpha\beta}$ does not contribute to the pressure or to the surface tension. A partial remedy to such a situation was introduced by Shan and Chen and other authors [33–35]. To take into account the contribution of the interactions to the equation of state they included a self-consistent term, named the pseudo-potential. This ad-hoc adjustment allowed to consider the hydrodynamic properties of non ideal gases by means of the so-called Lattice Boltzmann method (LBM) [19]. The pseudo-potential is a conservative force and does not determine the transport coefficients, which only depend on the adjustable parameters $\omega_{\alpha\beta}$. In the language of the present article the Shan-Chen method is a particular choice of $\mathbf{G}^{\alpha\beta}$ with the peculiarity that it contains both attractive and repulsive contributions, an assumption which is somehow in conflict with the standard methods of liquid state theory, where one treats separately and on a different basis attractive and repulsive forces [36].

The full collision RET operator (5) being a non-linear functional of f^α , couples the different velocity moments of the distributions thus rendering analytic work very hard, unless one adopts a suitable truncation scheme.

Any satisfactory approximation must retain the physical symmetries and conservation laws which are incorporated in the microscopic representation (5) and (7). To achieve that goal Dufty et al. [37, 38] separated the contributions of $\Omega^{\alpha\beta}$ to the hydrodynamic equations from those affecting the evolution of non-hydrodynamic modes, by projecting the collision term onto the hydrodynamic subspace spanned by the functions $\{1, \mathbf{v}, v^2\}$ and onto the complementary kinetic subspace:

$$\Omega^{\alpha\beta} = \mathcal{P}_{hydro}\Omega^{\alpha\beta} + (I - \mathcal{P}_{hydro})\Omega^{\alpha\beta} \quad (15)$$

with

$$\mathcal{P}_{hydro}\Omega^{\alpha\beta}(\mathbf{r}, \mathbf{v}, t) \equiv \frac{1}{k_B T(\mathbf{r}, t)} \frac{\psi^\alpha(\mathbf{r}, \mathbf{v}, t)}{n^\alpha(\mathbf{r}, t)} \begin{pmatrix} 0 \\ (\mathbf{v} - \mathbf{u}) \cdot \mathbf{C}^{\alpha\beta}(\mathbf{r}, t) \\ (\frac{m^\alpha(\mathbf{v} - \mathbf{u})^2}{3k_B T(\mathbf{r}, t)} - 1)B^{\alpha\beta}(\mathbf{r}, t) \end{pmatrix} \quad (16)$$

and

$$\begin{pmatrix} 0 \\ \mathbf{C}^{\alpha\beta}(\mathbf{r}, t) \\ B^{\alpha\beta}(\mathbf{r}, t) \end{pmatrix} = \int d\mathbf{v} \begin{pmatrix} 1 \\ m^\alpha(\mathbf{v} - \mathbf{u}) \\ \frac{m^\alpha(\mathbf{v} - \mathbf{u})^2}{2} \end{pmatrix} \Omega^{\alpha\beta}(\mathbf{r}, \mathbf{v}, t). \quad (17)$$

The vanishing of the first element of the array in the l.h.s of eq. (17) expresses the conservation law of the number of particles of each species in a collision.

Due to the splitting (15), the orthogonal part of the collision term will not appear explicitly in the balance equations for the hydrodynamic variables (see eqs. (20)-(23)). This fact suggests a simple approximation for $(I - \mathcal{P}_{hydro})\Omega^{\alpha\beta}$, where one replaces the exact expression by a BGK-like relaxation time term, having the property of vanishing under the application of the operator \mathcal{P}_{hydro} :

$$\sum_{\beta} (I - \mathcal{P}_{hydro})\Omega^{\alpha\beta}(\mathbf{r}, \mathbf{v}, t) \simeq -\omega[f^\alpha(\mathbf{r}, \mathbf{v}, t) - \psi_\perp^\alpha(\mathbf{r}, \mathbf{v}, t)], \quad (18)$$

where ω is a relaxation frequency and

$$\begin{aligned} \psi_\perp^\alpha(\mathbf{r}, \mathbf{v}, t) = \psi^\alpha(\mathbf{r}, \mathbf{v}, t) & \left\{ 1 + \frac{m^\alpha(\mathbf{u}^\alpha(\mathbf{r}, t) - \mathbf{u}(\mathbf{r}, t)) \cdot (\mathbf{v} - \mathbf{u}(\mathbf{r}, t))}{k_B T(\mathbf{r}, t)} \right. \\ & \left. + \frac{m^\alpha}{2k_B T(\mathbf{r}, t)} \left(\frac{m^\alpha[(\mathbf{u}^\alpha(\mathbf{r}, t) - \mathbf{u}(\mathbf{r}, t)) \cdot (\mathbf{v} - \mathbf{u}(\mathbf{r}, t))]^2}{k_B T(\mathbf{r}, t)} - (\mathbf{u}^\alpha(\mathbf{r}, t) - \mathbf{u}(\mathbf{r}, t))^2 \right) \right\}. \end{aligned} \quad (19)$$

The factor multiplying the Maxwellian in eq. (19) serves as to "orthogonalize" the term $-\omega[f^\alpha - \psi_\perp^\alpha]$ to the collisional terms proportional to \mathbf{C} and B , so that the BGK contribution does not explicitly affect the balance equations.

We construct, now, the hydrodynamic equations by projecting the equations (1) onto the hydrodynamic subspace. Multiplying by $\{1, m^\alpha \mathbf{v}, m^\alpha(\mathbf{v} - \mathbf{u})^2/2\}$, integrating over velocity and summing over components, we obtain the following set of balance equations:

$$\partial_t \rho(\mathbf{r}, t) + \nabla \cdot (\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)) = 0, \quad (20)$$

which represents the continuity law of the mass density. In addition we have the continuity equations for each species:

$$\partial_t \rho^\alpha(\mathbf{r}, t) + \nabla \cdot (\rho^\alpha(\mathbf{r}, t) \mathbf{u}^\alpha(\mathbf{r}, t)) = 0. \quad (21)$$

We also find the momentum balance equation

$$\begin{aligned} & \partial_t [\rho(\mathbf{r}, t) u_j(\mathbf{r}, t)] + \nabla_i (\rho(\mathbf{r}, t) u_i(\mathbf{r}, t) u_j(\mathbf{r}, t)) \\ & = -\nabla_i P_{ij}^{(K)}(\mathbf{r}, t) + \sum_{\alpha} \frac{F_j^\alpha(\mathbf{r})}{m^\alpha} \rho^\alpha(\mathbf{r}, t) + \sum_{\alpha\beta} C_j^{\alpha\beta}(\mathbf{r}, t) \end{aligned} \quad (22)$$

and the balance equation for the local temperature:

$$\begin{aligned} & \frac{3}{2}k_B n(\mathbf{r}, t) \left(\partial_t + u_i(\mathbf{r}, t) \nabla_i \right) T(\mathbf{r}, t) \\ &= -P_{ij}^{(K)}(\mathbf{r}, t) \nabla_i u_j(\mathbf{r}, t) - \nabla_i q_i^{(K)}(\mathbf{r}, t) + B(\mathbf{r}, t) + \sum_{\alpha} \rho^{\alpha}(\mathbf{r}, t) \frac{F_i^{\alpha}(\mathbf{r})}{m^{\alpha}} (u_i^{\alpha}(\mathbf{r}, t) - u_i(\mathbf{r}, t)), \end{aligned} \quad (23)$$

with $B = \sum_{\alpha\beta} B^{\alpha\beta}$, where we have introduced the kinetic part of the pressure tensor:

$$P_{ij}^{(K)}(\mathbf{r}, t) = \sum_{\alpha} m^{\alpha} \int d\mathbf{v} (v_i^{\alpha} - u_i)(v_j^{\alpha} - u_j) f^{\alpha}(\mathbf{r}, \mathbf{v}, t) \quad (24)$$

and the kinetic part of the heat flux vector

$$\mathbf{q}^{(K)} \equiv \sum_{\alpha} m^{\alpha} \int d\mathbf{v} (\mathbf{v} - \mathbf{u}) \frac{(\mathbf{v} - \mathbf{u})^2}{2} f^{\alpha}(\mathbf{r}, \mathbf{v}, t). \quad (25)$$

Eqs. (22) and (23) assume their standard hydrodynamic form, if we insert the relation (see ref.[37]) between the collisional moments and the divergence of the collisional transfer contribution to the pressure:

$$\nabla_i P_{ij}^{(C)}(\mathbf{r}, t) = - \sum_{\alpha\beta} C_j^{\alpha\beta}(\mathbf{r}, t) \quad (26)$$

and the relation between the collisional transfer contribution to the heat flux and the pressure:

$$\nabla_i q_i^{(C)}(\mathbf{r}, t) + P_{ij}^{(C)}(\mathbf{r}, t) \nabla_i u_j(\mathbf{r}, t) = -B(\mathbf{r}, t). \quad (27)$$

Notice two facts: a) at equilibrium the term (18) vanishes, b) out of equilibrium it determines a fast relaxation of the distributions towards the local values of $\mathbf{u}(\mathbf{r}, t)$ and $T(\mathbf{r}, t)$.

In order to obtain explicit expressions for \mathbf{C} and B we make a further approximation. We perform the integrals appearing in eq.(17) by replacing the true distribution functions $f^{\alpha}(\mathbf{r}, \mathbf{v}, t)$ by the Maxwellian distributions, corresponding to average density $n^{\alpha}(\mathbf{r}, t)$, local velocity $\mathbf{u}^{\alpha}(\mathbf{r}, t)$ and temperature $T(\mathbf{r}, t)$. Many years ago the same kind of approximation was used by Longuet-Higgins and Pople [39] to predict the transport coefficients of hard core systems. As shown in ref. [22] a useful representation of the last term in eq. (22) is obtained by the following decomposition:

$$\sum_{\beta} \mathbf{C}^{\alpha\beta}(\mathbf{r}, t) = n^{\alpha}(\mathbf{r}, t) \left(\mathbf{F}^{\alpha, mf}(\mathbf{r}, t) + \mathbf{F}^{\alpha, drag}(\mathbf{r}, t) + \mathbf{F}^{\alpha, viscous}(\mathbf{r}, t) + \mathbf{F}^{\alpha, T}(\mathbf{r}, t) \right). \quad (28)$$

The first term in the r.h.s. can be identified with the force acting on the α -particles at \mathbf{r} due to the influence of all remaining particles in the system, the gradient of the potential of mean force:

$$\mathbf{F}^{\alpha, mf}(\mathbf{r}, t) = -k_B T \sum_{\beta} \sigma_{\alpha\beta}^2 \int d\hat{\mathbf{s}} \hat{\mathbf{s}} g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) n_{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) + \sum_{\beta} \mathbf{G}^{\alpha\beta}(\mathbf{r}, t), \quad (29)$$

where the integral over $\hat{\mathbf{s}}$ is over the surface of a unit sphere. The second term is the average drag force experienced by particles of species α when moving with velocity u^{α} with respect to the remaining species having velocities u^{β} :

$$\begin{aligned} \mathbf{F}^{\alpha, drag}(\mathbf{r}, t) &= - \sum_{\beta} 2\sigma_{\alpha\beta}^2 \sqrt{\frac{2\mu_{\alpha\beta} k_B T(\mathbf{r}, t)}{\pi}} \times \\ & (\mathbf{u}^{\alpha}(\mathbf{r}, t) - \mathbf{u}^{\beta}(\mathbf{r}, t)) \cdot \int d\hat{\mathbf{s}} \hat{\mathbf{s}} g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) n^{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t), \end{aligned} \quad (30)$$

where $\mu_{\alpha\beta}$ is the reduced mass: $\mu_{\alpha\beta} = (m^{\alpha} m^{\beta}) / (m^{\alpha} + m^{\beta})$. The third term is a viscous force due to the presence of gradients in the velocity field:

$$\begin{aligned} \mathbf{F}^{\alpha, viscous}(\mathbf{r}, t) &= \sum_{\beta} 2\sigma_{\alpha\beta}^2 \sqrt{\frac{2\mu_{\alpha\beta} k_B T(\mathbf{r}, t)}{\pi}} \times \\ & \int d\hat{\mathbf{s}} \hat{\mathbf{s}} g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) n^{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) \hat{\mathbf{s}} \cdot (\mathbf{u}^{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}) - \mathbf{u}^{\beta}(\mathbf{r})), \end{aligned} \quad (31)$$

while the last term takes into account the contribution to the force due to temperature gradients:

$$\mathbf{F}^{\alpha,T}(\mathbf{r},t) = - \sum_{\beta} \frac{m^{\alpha}}{m^{\alpha} + m^{\beta}} \sigma_{\alpha\beta}^2 \int d\hat{\mathbf{s}} \hat{\mathbf{s}} g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) \times n^{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) k_B [T(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) - T(\mathbf{r}, t)]. \quad (32)$$

Finally, the energy integrals are given by the expression:

$$\begin{aligned} B(\mathbf{r},t) = & k_B T(\mathbf{r},t) \sum_{\alpha\beta} \sigma_{\alpha\beta}^2 \int d\hat{\mathbf{s}} g_{\alpha\beta}(\mathbf{r}, \mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) n^{\alpha}(\mathbf{r},t) n^{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) \times \\ & \left[-\frac{m^{\beta}}{m^{\alpha} + m^{\beta}} \hat{\mathbf{s}} \cdot [\mathbf{u}^{\beta}(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) - \mathbf{u}^{\beta}(\mathbf{r},t)] - \frac{m^{\beta}}{m^{\alpha} + m^{\beta}} \hat{\mathbf{s}} \cdot [\mathbf{u}^{\beta}(\mathbf{r},t) - \mathbf{u}(\mathbf{r},t)] \right. \\ & \left. - \frac{m^{\alpha}}{m^{\alpha} + m^{\beta}} \hat{\mathbf{s}} \cdot [\mathbf{u}^{\alpha}(\mathbf{r},t) - \mathbf{u}(\mathbf{r},t)] + \frac{2}{m^{\alpha} + m^{\beta}} \sqrt{\frac{2\mu_{\alpha\beta} k_B T(\mathbf{r},t)}{\pi}} \frac{[T(\mathbf{r} + \sigma_{\alpha\beta} \hat{\mathbf{s}}, t) - T(\mathbf{r},t)]}{T(\mathbf{r},t)} \right] \\ & + n^{\alpha}(\mathbf{r},t) \mathbf{G}^{\alpha\beta}(\mathbf{r},t) \cdot \mathbf{w}^{\alpha}(\mathbf{r},t), \end{aligned} \quad (33)$$

where $\mathbf{w}^{\alpha}(\mathbf{r},t) = \mathbf{u}^{\alpha}(\mathbf{r},t) - \mathbf{u}(\mathbf{r},t)$. Notice that eq. (28) represents a decomposition of the total force in dissipative and non dissipative terms. The first (eq. (29)) and the fourth term (eq. (32)) are non dissipative and have opposite sign under time-reversal with respect to the partial momentum current $n^{\alpha} \mathbf{u}^{\alpha}$, that they induce via the balance equation eq. ((22)). The dissipative terms eq.(30) and eq.(31), instead, have the same parity as the current [40]. Moreover, dissipative forces have an equilibrium counterpart, being related, as shown in ref.[23], to the intrinsic chemical potential of the individual components:

$$\mathbf{F}^{\alpha,mf}(\mathbf{r},t) = -\nabla \mu_{int}^{\alpha}(\mathbf{r},t), \quad (34)$$

while dissipative forces vanish at equilibrium. Eq. (34) represents a direct connection between the effective force featuring in the DDFT and the present approach and this fact opens the possibility of transferring to systems out of equilibrium the vast knowledge accumulated in the last twenty years concerning effective interactions in colloidal solutions and liquid mixtures at equilibrium [41–43]. On the other hand, the dissipative forces cannot be derived from a functional derivative of the Helmholtz free energy functional, $\mathcal{F}(\{n^{\alpha}\})$. In other words, the DDFT does not give information about the transport coefficients of the system, which are originated by non-equilibrium processes not accounted for by this approach.

Once the self-consistent fields \mathbf{C} and B have been specified, it is possible to solve eqs. (1) and study fluids under a variety of inhomogeneous conditions, using the LBM to achieve a numerical solution of eq. (1). We have shown in a recent series of papers that the main features of a structured fluid can be captured up to moderate packing fraction [23] by a suitable extension of the LBM. In the present paper we shall not discuss the numerical aspects of the problem, but investigate further some theoretical issues.

III. EQUILIBRIUM AND NON EQUILIBRIUM PROPERTIES OF BULK SYSTEMS

In order to recover the thermodynamic properties we impose the conditions of global equilibrium. These require that all the velocities u^{α} are equal and all hydrodynamic fields are time independent and, with the exception of the densities n^{α} , are spatially uniform. With $T = \text{constant}$ $\mathbf{u}^{\alpha} = \text{constant}$, eq. (22), the momentum balance condition, reduces to the hydrostatic equilibrium condition. The r.h.s. of eq. (26) relating the equilibrium part of the potential contributions to the pressure tensor can be separated into a repulsive, $P_{ij}^{rep}(\mathbf{r},t)$ and an attractive term $P_{ij}^{attr}(\mathbf{r},t)$. The pressure can be obtained by applying the following formulae originally derived by Kirkwood [37, 44].

$$\begin{aligned} P_{ij}^{rep}(\mathbf{r},t) = & \sum_{\alpha\beta} \frac{k_B T}{2} \sigma_{\alpha\beta}^3 \int d\hat{\mathbf{s}} \hat{s}_i \hat{s}_j \times \\ & \int_0^1 d\lambda g_{\alpha\beta}(\mathbf{r} - (1-\lambda)\sigma_{\alpha\beta} \hat{\mathbf{s}}, \mathbf{r} + \lambda\sigma_{\alpha\beta} \hat{\mathbf{s}}) n^{\alpha}(\mathbf{r} - (1-\lambda)\sigma_{\alpha\beta} \hat{\mathbf{s}}) n^{\beta}(\mathbf{r} + \lambda\sigma_{\alpha\beta} \hat{\mathbf{s}}) \end{aligned} \quad (35)$$

and

$$P_{ij}^{attr}(\mathbf{r}, t) = - \sum_{\alpha\beta} \frac{1}{2} \int d^d R \frac{R_i R_j}{R} \frac{\partial U_{attr}^{\alpha\beta}(R)}{\partial R} \times \int_0^1 d\lambda g_{\alpha\beta}(\mathbf{r} + (1-\lambda)\mathbf{R}, \mathbf{r} - \lambda\mathbf{R}) n^\alpha(\mathbf{r} + (1-\lambda)\mathbf{R}) n^\beta(\mathbf{r} - \lambda\mathbf{R}).$$

In the case of a uniform system the total bulk pressure, P^{bulk} , obtained by summing the kinetic and potential contributions and taking all the fields to be constant, is diagonal and isotropic:

$$P^{bulk} = k_B T \sum_{\alpha} n^{\alpha} \left(1 + \frac{2\pi}{3} \sum_{\beta} \sigma_{\alpha\beta}^3 n^{\beta} g_{\alpha\beta}(\sigma_{\alpha\beta}) - \frac{2\pi}{3k_B T} \sum_{\beta} n^{\beta} \int dR R^3 g_{\alpha\beta}(R) \frac{\partial U_{attr}^{\alpha\beta}(R)}{\partial R} \right). \quad (36)$$

In addition, the surface tension of a planar interface can be calculated from Kirkwood and Buff formula [7],

$$\gamma = \int_{-\infty}^{\infty} dz [P_N(z) - P_T(z)], \quad (37)$$

where the subscripts N and T indicate normal and tangential components of the pressure tensor, respectively.

Non equilibrium properties. The kinetic coefficients can be considered to be the sum of two contributions: the first due to the instantaneous transmission of momentum and energy across the bodies of molecules upon collision and the second resulting from the distortion of the Maxwell-Boltzmann distribution induced by the presence of viscous and heat flows. Hereafter, we briefly report the calculation of the kinetic coefficients along lines similar to those discussed in ref. [21].

Collisional contributions to transport coefficients. While kinetic transport, prevailing at low densities, is originated by the movement of the particles carrying a certain amount of momentum and energy, collisional transport, dominant at higher densities, is due to the transfer of momentum and energy from one particle to the other during collisions. Following steps similar to those of references [20, 21], we derive the collisional shear viscosity and heat conductivity of the mixture. To simplify the derivation we assume that the densities and the temperature are uniform, $n_A, n_B = \text{const}$ and $T(\mathbf{r}, t) = T_0$ and $\mathbf{u}^\alpha = \mathbf{u}^\beta = \mathbf{u}$ and that the velocity field is a shear slowly varying over distances of the order of the molecular diameter:

$$\mathbf{u}(\mathbf{r}, t) = (0, u_y(x, 0), 0). \quad (38)$$

We compute the collisional contribution to the viscosity using the relation:

$$\sum_{\alpha\beta} C_y^{\alpha\beta} = - \frac{\partial P_{xy}^{(C)}}{\partial x} = \eta^{(C)} \frac{\partial^2 u_y}{\partial x^2} \quad (39)$$

where we employed eq. (26) for the first equality and the constitutive relation

$$P_{xy}^{(C)} = P_{yx}^{(C)} = -\eta^{(C)} \left[\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right] \quad (40)$$

for the second equality. With the help of eqs. (28) and (31), after expanding to second order in $\sigma_{\alpha\beta}$, we obtain:

$$\eta^{(C)} = \frac{4}{15} \sum_{\alpha\beta} \sqrt{2\pi\mu_{\alpha\beta} k_B T} \sigma_{\alpha\beta}^4 g_{\alpha\beta} n^\alpha n^\beta. \quad (41)$$

Similarly, if we assume $n^\alpha = \text{constant}$, $\mathbf{u}^\alpha = \mathbf{u}^\beta$ and small temperature gradients, we can derive the thermal conductivity. We use the constitutive relation

$$\mathbf{q}^{(C)}(\mathbf{r}, t) = -\lambda^{(C)} \nabla T(\mathbf{r}, t), \quad (42)$$

compare with relation (27) and expand $B(\mathbf{r}, t)$ (formula (33)) to second order in $\sigma_{\alpha\beta}$ with the result:

$$\lambda^{(C)} = \frac{4}{3} k_B \sqrt{2k_B T \pi} \sum_{\alpha\beta} \frac{\sqrt{\mu_{\alpha\beta}}}{m^\alpha + m^\beta} \sigma_{AB}^4 g_{\alpha\beta} n^\alpha n^\beta. \quad (43)$$

The present results are consistent with the theory of transport coefficients put forward for mono-disperse hard-sphere systems by Longuet-Higgins and Pople more than half a century ago [39]. It is based on the fact that in hard sphere systems even a local Maxwellian approximation to the distribution functions is able to account for the collisional transfer contribution to the transport coefficients. According to formulae (41) and (43) it is clear that within the present approximation the mean field term, $\mathbf{G}^{\alpha\beta}$, does not contribute to the transport coefficients.

Kinetic contributions to transport coefficients. The self-consistent Longuet-Higgins and Pople gaussian approximation employed above gives an expression for the transport coefficients at high densities, but does not give an expression for the kinetic contribution to these quantities. In order to obtain the full expression of the transport coefficients we apply the Chapman-Enskog analysis [32]. The kinetic contribution to the transport coefficients can be derived upon neglecting the interaction terms \mathbf{C} and B in the transport equation. The solution of the transport equation (1) can be written as:

$$f^\alpha(\mathbf{r}, \mathbf{v}, t) \approx \psi^\alpha(\mathbf{r}, \mathbf{v}, t) + \delta f^\alpha(\mathbf{r}, \mathbf{v}, t) \quad (44)$$

In this case eq.(1) to first order in δf^α reads:

$$\left(\partial_t + \mathbf{v} \cdot \nabla + \frac{\mathbf{F}^\alpha(\mathbf{r})}{m^\alpha} \cdot \frac{\partial}{\partial \mathbf{v}} \right) \psi^\alpha(\mathbf{r}, \mathbf{v}, t) = -\omega \delta f^\alpha(\mathbf{r}, \mathbf{v}, t). \quad (45)$$

Substituting (44) into (45) and taking the appropriate velocity moments we obtain the following Euler-like (i.e. without dissipative effects) hydrodynamic equations for the mixture. These are: the continuity equation for each species

$$\frac{\partial n^\alpha}{\partial t} + \frac{\partial(n^\alpha u_j)}{\partial x_j} = 0, \quad (46)$$

the global momentum conservation:

$$\sum_\alpha m^\alpha n^\alpha \left[\frac{\partial u_j}{\partial t} + u_i \frac{\partial u_j}{\partial x_i} \right] = - \frac{\partial P_{ij}}{\partial x_i} + \sum_\alpha F_{\alpha j}(\mathbf{r}) n^\alpha(\mathbf{r}, t), \quad (47)$$

and the temperature equation:

$$\sum_\alpha n^\alpha(\mathbf{r}, t) \left(\frac{\partial T}{\partial t} + u_i \frac{\partial T}{\partial x_i} \right) = - \sum_\alpha \frac{2}{3} n^\alpha(\mathbf{r}, t) T \frac{\partial u_i}{\partial x_j} \delta_{ij}. \quad (48)$$

Using again the solution (44) in eq. (45) and eliminating the time derivatives of the hydrodynamic fields with the help of eqs. (46)-(48) we obtain the first order correction to the distribution function:

$$\begin{aligned} \delta f^\alpha(\mathbf{r}, \mathbf{v}, t) = & -\frac{1}{\omega} \psi^\alpha \left\{ \frac{(v_i - u_i)}{k_B T} \left(\frac{m^\alpha}{\sum_\alpha m^\alpha n^\alpha} \left[-\frac{\partial P_{ij}}{\partial x_j} + \sum_\alpha F_{\alpha i} n^\alpha \right] + \frac{1}{n^\alpha} \frac{\partial(k_B T n^\alpha)}{\partial x_i} - F_i^\alpha \right) \right. \\ & \left. + \frac{m^\alpha}{k_B T} \left((v_i - u_i)(v_j - u_j) - \frac{1}{3} (\mathbf{v} - \mathbf{u})^2 \delta_{ij} \right) \frac{\partial u_i}{\partial x_j} + \left(m^\alpha \frac{(\mathbf{v} - \mathbf{u})^2}{2} - \frac{5}{2} k_B T \right) \frac{(v_i - u_i)}{k_B T^2} \frac{\partial T}{\partial x_i} \right\}, \end{aligned} \quad (49)$$

where the first term contributes to the diffusive current, the second term to the viscous flow and the third to the heat flow. With the help of eq. (49), we compute the off diagonal part of the kinetic stress tensor ($i \neq j$):

$$P_{ij}^{(K)} = \sum_\alpha m^\alpha \int d\mathbf{v} \delta f^\alpha(\mathbf{r}, \mathbf{v}, t) [(v_i - u_i)(v_j - u_j)] = -\eta^{(K)} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \sum_l \frac{\partial u_l}{\partial x_l} \right) \quad (50)$$

where the kinetic viscosity of the mixture is

$$\eta^{(K)} = \frac{k_B T}{\omega} \sum_\alpha n^\alpha. \quad (51)$$

Finally, we obtain the kinetic contribution to the heat flux

$$\mathbf{q}^{(K)} \equiv \sum_\alpha m^\alpha \int d\mathbf{v} (\mathbf{v} - \mathbf{u}) \frac{(\mathbf{v} - \mathbf{u})^2}{2} \delta f^\alpha(\mathbf{r}, \mathbf{v}, t) = -\lambda^{(K)} \nabla T, \quad (52)$$

where the kinetic contribution to the heat conductivity is:

$$\lambda^{(K)} = \frac{5k_B^2 T}{2\omega} \sum_\alpha \frac{n^\alpha}{m^\alpha}. \quad (53)$$

IV. HEURISTIC DERIVATION DDFT FROM HYDRODYNAMICS OF AN ASYMMETRIC BINARY MIXTURE

Classical dynamic density functional theory (DDFT) is a widely used tool for studying the dynamics of suspensions of colloidal particles in a solvent [45–49]. Within this approach only the density of the colloidal particles appears explicitly, whereas the solvent appears through the friction coefficient, or friction tensor. As a little remark, we wish to show that in the case of an isothermal hard sphere mixture in which the c (for colloidal) component is very diluted and the s (for solvent) particles are light ($m^s/m^c \ll 1$) it is possible to derive an equation for the density of species c , which is a special instance of the DDFT equation.

Being lighter, the s particles have higher thermal velocities and reach equilibrium faster. It is possible to integrate out their degrees of freedom and represent their influence by a viscous drag force, proportional to the velocity of the solute particles, plus a random force mimicking the effect of their random motions.

From the continuity equation (21) for the density of c particles we have:

$$\partial_t \rho^c(\mathbf{r}, t) + \nabla \cdot (\mathbf{u}(\mathbf{r}, t) \rho^c(\mathbf{r}, t)) + \nabla \cdot \frac{\rho^c(\mathbf{r}, t) \rho^s(\mathbf{r}, t)}{\rho(\mathbf{r}, t)} (\mathbf{u}^c(\mathbf{r}, t) - \mathbf{u}^s(\mathbf{r}, t)) = 0, \quad (54)$$

where we separated the advection term from the diffusion term, and \mathbf{u}^c and \mathbf{u}^s are the velocity of the colloidal particles and of the solvent, respectively. We now assume that the inertial term in the momentum equation for the colloidal particles can be neglected with respect to the molecular forces and the motion is not accelerated. In other words, we consider a low Reynolds number regime and obtain:

$$-\frac{k_B T}{n^c(\mathbf{r}, t)} \nabla n^c(\mathbf{r}, t) + \mathbf{F}^c(\mathbf{r}, t) + \mathbf{F}^{c,mf}(\mathbf{r}, t) + \mathbf{F}^{c,drag}(\mathbf{r}, t) + \mathbf{F}^{c,visc}(\mathbf{r}, t) \simeq 0 \quad (55)$$

where we used eq. (28). If, in addition, we neglect the shear force, with the help of eqs. (30) and (55) we eliminate the drag force in favour of $(\mathbf{u}^c - \mathbf{u}^s)$:

$$\begin{aligned} & (\mathbf{u}^c(\mathbf{r}, t) - \mathbf{u}^s(\mathbf{r}, t)) \simeq \\ & -\frac{3}{8\rho} \frac{m^s}{(2\pi\mu_{cs}k_B T)^{1/2}\sigma_{cs}^2 g_{cs}} \left(k_B T \nabla \ln n^c(\mathbf{r}, t) - \mathbf{F}^{c,mf}(\mathbf{r}, t) - \mathbf{F}^c(\mathbf{r}, t) \right). \end{aligned} \quad (56)$$

We define the local chemical potential, $\mu^c(\mathbf{r}, t)$, as the sum of the internal forces (see ref. [23]):

$$\nabla \mu^c(\mathbf{r}, t) = k_B T \nabla \ln n^c(\mathbf{r}, t) - \mathbf{F}^{c,mf}(\mathbf{r}, t),$$

substitute into the advection-diffusion equation (54), and take the diluted limit $n^c/n^s \ll 1$ and $\mathbf{u} \simeq \mathbf{u}^s$:

$$\partial_t n^c(\mathbf{r}, t) + \nabla \cdot (\mathbf{u}(\mathbf{r}, t) n^c(\mathbf{r}, t)) = \frac{1}{\gamma} \nabla \cdot \left[n^c(\mathbf{r}, t) \left(\nabla \mu^c(\mathbf{r}, t) - \mathbf{F}^c(\mathbf{r}, t) \right) \right], \quad (57)$$

where the friction coefficient, γ , is given by the expression:

$$\frac{1}{\gamma} = \frac{3}{8n^s} \frac{1}{\sqrt{\pi m^s k_B T} \sigma_{cs}^2 g_{cs}}. \quad (58)$$

We, now, observe that eq.(57) is formally identical to a DDFT equation for the c species in a velocity field $\mathbf{u}(\mathbf{r}, t)$. As $n^c \rightarrow 0$ the gradient of the chemical potential μ^c approaches the ideal gas value, $k_B T \nabla \ln n^c(\mathbf{r}, t)$, so that eq. (57) becomes a linear advection-diffusion equation for the field n^c , with a diffusion coefficient given by:

$$D = \frac{k_B T}{\gamma}, \quad (59)$$

to be interpreted as a fluctuation-dissipation relation between γ and D . Apparently, such a result sounds correct, appealing and satisfactory, but contradicts Einstein's theory of Brownian motion stating that the diffusion coefficient for a large and massive solute molecule of diameter σ_{cc} immersed in a solvent of much smaller and lighter molecules is related to the solvent viscosity by the Stokes-Einstein relation:

$$D_{SE} = \frac{k_B T}{\gamma_{hydro}}. \quad (60)$$

Einstein's theory relies on the hypothesis that a diffusing spherical body moves among solute particles as a macroscopic sphere does in a viscous incompressible continuum fluid. One first needs to solve the Stokes equation for the flow of the fluid around the sphere, with the condition of no slip at its surface. From the flow one computes the total stress acting on the sphere surface and finally the drag force, which results proportional to the (hydrodynamic) radius, $\sigma_{cc}/2$, of the object and to the viscosity, η_s , of the solvent according to the Stokes formula:

$$\mathbf{F}^{c,drag} = -\gamma_{hydro}(\mathbf{u}^c - \mathbf{u}) = -3\pi\eta_s\sigma_{cc}(\mathbf{u}^c - \mathbf{u}). \quad (61)$$

The Enskog relation (58) and the Stokes-Einstein relation (61) display different scalings with respect to the physical properties of the c particles. The relation

$$\gamma_{hydro} = 3\pi\eta_s\sigma_{cc}$$

for the friction coefficient shows a linear dependence on the solute diameter σ_{cc} , but no dependence on its mass, while the Enskog approximation considerably underestimates the friction coefficient, which depends on the reduced mass of the solute-solvent pair and has a quadratic dependence on the solute diameter. Only for very heavy solutes the mass dependence of Enskog friction coefficient vanishes (see eq. (56)). The numerically computed friction coefficient shows a crossover to the Stokes-Einstein result only for large values of the mass ratio at fixed size ratio. A full merging between the two approaches, in spite of repeated attempts, has not been achieved so far [50–52].

Clearly, the Enskog microscopic picture, where the interactions occur via collisions with the solvent particles, and the Einstein picture, which treats the solvent molecules as a continuum and the effect of the solute-solvent interactions by means of the no slip boundary condition, account for different mechanisms. Einstein's theory is correct for large solute particles, where the typical ratios between the radii of suspended colloidal particles and solvent molecules range in the interval 30 – 3000 and the mass ratio is in the interval $10^4 - 10^{10}$. These large differences justify the idea of complete separation of time scale between the motion of the solute, which occurs in a time of the order of $\tau_c = m^c/(3\pi\eta^s\sigma_{cc})$, and the motion of the solvent characterized by the Enskog collision time $\tau_s \simeq n^s\sigma_{ss}^2\sqrt{k_B T/m^s}$, the first being 5 orders of magnitude larger [53]. However, for small colloids the collisional and hydrodynamic regimes are not well separated. A crossover should occur when the size and the mass of the solute become comparable to those of the solvent molecules. In this case eq. (61) is not expected to be valid. The short time direct collisions between the tracer particle and the solvent particles are indeed taken into account by Enskog's theory, which, however, misses the long time behavior determined by correlated re-collisions of the tracer with the same solvent molecule [54]. The velocity auto-correlation function (VACF) of the c particles in Enskog's theory displays an exponential decay which is valid in the short time region, but does not show the algebraic inverse power law tails characterizing the long time behavior of the VACF. The pure exponential behavior is the result of the molecular-chaos assumption, i.e. of a Markovian representation of the dynamics, well describing the large mean free path regime. The RET is able to capture the formation of positional correlations, but not the build-up of velocity correlations among the particles, at the origin of the Stokes-Einstein behavior of the diffusion coefficient. It is our opinion that methods, which truncate the BBGKY hierarchy at the level of one-particle distribution functions, are not apt to account for the renormalization of the transport coefficients due to the presence of velocity correlations, the ultimate cause of hydrodynamic interactions. With respect to this problem mode coupling theory (MCT) is able to predict the correct behavior by including at the same time binary collision processes, coupling with transverse current of the solvent and with density fluctuations [55].

Finally, it is worth to mention that a simpler way to bridge Einstein with Enskog theory as the size or the colloids is reduced to that of the solvent particles has been described in ref. [24, 56], where the motion of the colloid is described by a Langevin equation with a friction coefficient which is non-local in time in order to reproduce a non Markovian behavior. Although, such an approach is frankly phenomenological it is able to predict the backscattering effect.

V. CONCLUSIONS

In this paper we have considered how microscopic methods, utilized to study the non-equilibrium evolution of colloidal solutions and well accounting for their configurational properties, can be extended to investigate the dynamics of liquid mixtures. We have adopted a strategy based upon kinetic methods and shown that the resulting equations correctly describe the hydrodynamic behavior of the density, momentum and energy transport. We have found similarities with the DDFT equations, and this not surprising since the common basic ingredient of both methods is the free energy which in one way or another features in the theory. In DDFT we directly use the free energy functional, and in the kinetic approach we employ its functional derivative, the inhomogeneous positional pair correlation function, $g(r, r')$. Finally, to link further the two descriptions we have introduced an heuristic derivation of the DDFT equation from the kinetic equations for a hard-sphere mixture. Our result seems to indicate the possibility of extending this procedure to mixture of higher physical interest.

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